

useful in studies of the Coster-Kronig decay of M_1 and $M_{2,3}$ holes. However, at the present time, there are no experimental data known to the author on these low-energy transitions other than the poorly resolved data of Auger surface studies. For the

$M_{4,5}$ Auger spectra the only data available are for Kr and Xe, where purely $j-j$ coupling is not applicable. Comparison with the available data indicates reasonable agreement except for the $(4s, 4p)^1P_1$ term in Kr.

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Stark Effect in Alkali-Metal Ground-State Hyperfine Structure*

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An atomic-beam magnetic-resonance apparatus with separated oscillatory fields has been used to measure the decrease in the ground-state hyperfine energy separation of Cs^{133} , Rb^{87} , Rb^{85} , K^{39} , Na^{23} , and Li^7 because of the presence of a uniform, static, electric field. The hfs frequency shift due to this quadratic Stark effect is designated by $\delta f = -k \times 10^{-6} E^2 \text{ Hz}/(\text{V/cm})^2$. If the ratio $\delta f(X^A)/\delta f(\text{Cs}^{133})$ is denoted by κ_{XA} , then the results are $\kappa_{\text{Rb}^{87}} = 0.546(5)$; $\kappa_{\text{Rb}^{85}} = 0.243(1)$, $\kappa_{\text{K}^{39}} = 0.0315(6)$, $\kappa_{\text{Na}^{23}} = 0.0552(12)$, and $\kappa_{\text{Li}^7} = 0.0270(8)$. Existing theories of the alkali-metal Stark effect are discussed, and none is found to give satisfactory agreement with these experimental ratios.

INTRODUCTION

When an alkali-metal atom is placed in a static electric field, it sustains a decrease in its ground-state hyperfine-energy separation $h\Delta\nu$. The shift in the frequency of the $0 \rightarrow 0$ hfs transition $(I + \frac{1}{2}, 0) \rightarrow (I - \frac{1}{2}, 0)$ is given by

$$\delta f = -k \times 10^{-6} E^2 \text{ Hz}/(\text{V/cm})^2$$

so that the frequency shift is $-k \text{ Hz}$ in a field of 1 kV/cm. This quadratic Stark effect¹ (QSE) has been measured by the atomic-beam magnetic-resonance technique in cesium² and potassium³, and in the hydrogen maser.⁴ Except for cesium,⁵ discrepancies still exist between theory^{6,7} and experiment. The excellent agreement in the case of cesium suggests the possibility of using that atom as a reference to which other Stark shifts may be compared. Such comparisons are free from the experimental uncertainties in the electric field plate spacing and in the so called filling factor associated with the separated oscillatory field method. This paper describes measurements performed

on the $0 \rightarrow 0$ transition in Rb^{87} , Rb^{85} , K^{39} , Na^{23} (which have been reported previously⁸) and on Li^7 . No existing theory suffices to explain these shifts *quantitatively*.

THEORETICAL CONSIDERATIONS

Sandars⁷ has shown that the frequency shift of the $0 \rightarrow 0$ transition in the ground-state hfs of an alkali-metal atom in a uniform, static electric field can be written

$$\delta f = (-1/2Ih)[(2I+1)\alpha_{10} - \alpha_{12}]E^2,$$

where I is the nuclear spin in units of \hbar . The dominant contribution to δf comes from the (scalar) polarizability α_{10} which results from the hfs contact interaction

$$H_{10} = \frac{16\pi}{3} \frac{\mu_B \mu_I}{I} (\vec{I} \cdot \vec{s}) \delta(\vec{r})$$

acting on a $^2S_{1/2}$ state that is perturbed by an electric field. (\vec{s} is the electron spin angular momentum, μ_B the Bohr magneton, and μ_I the nuclear

magnetic dipole moment.) The smaller (tensor) polarizability α_{12} is due to the tensor part of the magnetic hfs interaction

$$H_{12} = \frac{2\mu_B\mu_I}{I} (3I_z s_z - \vec{I} \cdot \vec{S}) \frac{C_0^2}{r^3},$$

where C_0^2 is the modified spherical harmonic of rank two, projection zero.

Sandar's calculations of α_{10} and α_{12} involve radial wave functions and cannot be readily generalized to the alkali-metal atoms for two reasons: First, he uses an explicit hydrogen wave function for the field-free ground-state atom without hyperfine structure. Second, the perturbation method which he uses yields a closed solution only for the special case in which the unperturbed ground-state energy is exactly -1 Ry. It should be pointed out that when the nuclear electric quadrupole moment Q is known, the experiments of Gould *et al.*⁹ on the Zeeman transition $(I + \frac{1}{2}, -I - \frac{1}{2}) \leftrightarrow (I + \frac{1}{2}, -I + \frac{1}{2})$ provide experimental values for α_{12} according to

$$\delta f_{zee} = \frac{3}{h(2I+1)} \left(1 - \frac{Qe^2}{4\mu_B\mu_I} \right) \alpha_{12} E^2.$$

Those experiments, together with the previous measurements of the $0 \leftrightarrow 0$ transitions in Cs¹³³ and K³⁹ indicate that α_{12} is at most a few percent of $(2I+1)\alpha_{10}$.

Anderson⁶ has attempted to calculate the Stark effect for all the alkali metals in addition to hydrogen. His idea was to estimate the perturbed ground-state wave function ψ_0 and thence the change in the Fermi formula¹⁰ for the zero-field hfs separation

$$h\Delta\nu = \frac{8\pi}{3} \mu_B\mu_I \frac{2I+1}{I} |\psi_0(0)|^2.$$

His method, therefore, includes the contact hfs but not the tensor hfs interaction. He obtains

$$\delta f = -\alpha\Delta\nu E^2 \left[\frac{1}{2} (\bar{W}_{n'P}^0 - W_{nS}^0)^{-1} + (\bar{W}_{n'S}^0 \text{ or } n'D - W_{nS}^0)^{-1} \right],$$

where α is the atomic polarizability

$$\alpha \equiv e^2 \sum_{\text{all } P \text{ states}} \frac{\langle nS | z | n'P \rangle \langle n'P | z | nS \rangle}{W_{n'P}^0 - W_{nS}^0}$$

obtained from the electric dipole interaction ez when hfs effects are neglected, and W_{nS}^0 is the unperturbed ground-state energy. The denominators

$$\bar{W}_{n'P}^0 - W_{nS}^0 \quad \text{and} \quad \bar{W}_{n'S}^0 \text{ or } n'D - W_{nS}^0$$

are average-energy denominators that have been factored out of the infinite sums appearing in the expressions for the wave function ψ_0 and the polarizability α . Such factorization permits the evaluation of the infinite sums by the closure con-

dition.

The success of this method depends upon the ability to evaluate the average-energy denominators and upon the availability of accurate values for the polarizability α . In the case of hydrogen, Anderson was able to fix the denominator $\bar{W}_{n'P}^0 - W_{nS}$ through its dependence upon α . The choice $\bar{W}_{n'S}^0 \text{ or } n'D = W_{2S}^0$ led to a prediction of the Stark shift in hydrogen that is in good agreement with a later experiment.⁴ Lacking knowledge of the unperturbed ground-state wave functions of the alkali metals, Anderson chose the energies of the first excited P state and either the first excited S or D state, whichever was lower, for $\bar{W}_{n'P}^0$ and $\bar{W}_{n'S}^0 \text{ or } n'D$. The resulting good agreement with the Cs¹³³ measurement² turned out to have been fortuitous once revised experimental polarizabilities were published.¹¹

Feitchner, Hoover, and Mizushima⁵ use cesium wave functions to calculate the perturbation of the ground-state and the excited P -state wave functions due to the complete hfs interaction. This interaction is found to mix states of different principal quantum number, but with the same total angular momentum F and projection m_F . These perturbed wave functions are then used to evaluate the matrix elements in a second-order perturbation theory calculation which finds the change in energy of each ground-state hfs level because of the electric field. Their result¹² for $(4, 0) \leftrightarrow (3, 0)$

$$\delta f = -2.248 \times 10^{-6} E^2$$

is in excellent agreement with the cesium measurement²

$$\delta f = -2.29(3) \times 10^{-6} E^2.$$

This method could be adapted to the other alkalis as soon as accurate S - and P -state wave functions become available.

EXPERIMENT

A symmetrical atomic-beam magnetic-resonance apparatus employing separated oscillatory fields¹³ was used to measure the Stark shifts in Cs¹³³, Rb⁸⁷, Rb⁸⁵, K³⁹, Na²³, and Li⁷. The interaction ("C") region containing electric field plates, rf loops and shielded Helmholtz coil has been described elsewhere.⁹ Details of beam production and detection are omitted since standard methods were used.^{9,13}

An experimental run consisted of measuring the frequency of the $(I + \frac{1}{2}, 0) \leftrightarrow (I - \frac{1}{2}, 0)$ transition as a function of the voltage applied to the electric field plates for voltages ranging from about 10 to about 18 kV (electric fields ranging from about 38 to about 96 kV/cm.) A static magnetic field of about 150 mG applied parallel to the electric field isolated the $0 \leftrightarrow 0$ transition. The correct transition was readily identified among the other focusable hfs

TABLE I. Comparison of experimental and theoretical results, $^a \delta f = -k E^2 \times 10^{-6} \text{ Hz}/(\text{V}/\text{cm})^2$.

Isotope	κ_{meas}	κ_{HZ}	k	k_{meas}	k_A
Cs ¹³³	1.0000	1.0000	2.248 ^b	2.25(5)	3.78
Rb ⁸⁷	0.546(5)	0.491	1.227(11)	1.23(3)	1.66
Rb ⁸⁵	0.243(1)	0.218	0.546(2)	0.546(12)	0.737
K ³⁹	0.0315(6)	0.0304	0.071(1)	0.071(2)	0.099
Na ²³	0.0552(12)	0.0453	0.124(3)	0.124(4)	0.152
Li ⁷	0.0270(8)	0.0256	0.061(2)	0.061(2)	0.078

^aSee text for explanation of symbols.

^bReference 5.

transitions because of its relatively small field dependence near zero magnetic field (typically 20 kHz/G between 0 and 1 G). This weak field dependence together with the relatively large rf loop separation permitted linewidths as narrow as 400 Hz (cesium).

Data consisted of measured frequencies and measured voltages. Voltage-controlled frequency sources (e.g., varactor-tuned fundamental transistor oscillators and reflex klystrons), frequency synthesizer, and digital frequency counter were all stabilized by phase synchronization to an ultra-stable crystal oscillator. With a rated stability of four parts in 10^{10} /day, this crystal time base guaranteed frequency stability of 1 Hz at the largest frequency used (9192 MHz). When the beam noise was normal, transition frequencies could be determined to a precision of ± 20 Hz, or about $\frac{1}{40}$ of the linewidth of the fastest atom (Li⁷). The smallest shifts studied were on the order of $\frac{1}{4}$ the linewidth. The rated stability of the C magnet power supply, together with the low field dependence of the transition studied guaranteed that drifts in the resonance due to drifting C field were much less than 1 Hz over the few hours needed for a run.

High-voltage supplies (stability about 0.1% over 1 h) were calibrated using a precision divider and differential voltmeter, the stability of which was checked periodically by comparison with a standard cell.

Each measured frequency $f(V^2)$ for which $V^2 \neq 0$ yielded a value for

$$K = [f(V^2) - f(0)]/V^2.$$

At least 18 and sometimes more than 30 values of K were obtained, in successive runs, for each isotope studied. Changing the static magnetic field, the rf power level and the direction of the electric field had no observable effect on the K 's so determined. Values of K obtained for two different peaks of the two-loop interference pattern were within the usual spread of the measurements.

DISCUSSION OF RESULTS

The experimentally determined frequency shifts

K can be related to the desired shifts k by

$$k = K(s/l)d^2,$$

where l is the length of the electric field plates, d their separation and s is the separation of the rf loops. The uncertainties associated with l , s , and d contribute about 2% to the total uncertainty in k , whereas K can be determined to a precision of better than 1% in the best cases. In order to eliminate these systematic uncertainties from the results, the ratios

$$\kappa_{XA} = (K_{XA})/(K_{\text{Cs}133}) = (k_{XA})/(k_{\text{Cs}133}),$$

which involve only the uncertainties in the measurements of the K 's and are otherwise *independent* of the apparatus, are quoted as the results of these experiments. These results are listed in column 2 of Table I. The error is one standard deviation and is comprised of the standard deviation of K_{XA} and $K_{\text{Cs}133}$ combined in quadrature. These two standard deviations are determined solely from the spread of the K 's from run to run, and are about 100 times larger than the errors obtained by a least-squares fit to a straight line of frequency shift *versus* voltage squared. The percentage errors $\sigma(\kappa)/\kappa$ grow larger as one goes down the column for two reasons: First, the lighter atoms travel faster through the rf loops than do the heavier ones. Hence their interaction time with the oscillatory field is shorter, and their resonance linewidth is greater than for the slower atoms. Since it is more difficult to determine the center of a broad line compared to a narrow line, the measured frequencies are less precise. Second, the lighter atoms have smaller Stark shifts, and the least count of the digital frequency counter (± 10 Hz) can eventually be a sizable (6%) fraction of the shift.

Column 3 lists the ratios κ_{HZ} obtained by using the simple theory given in Ref. 2 and values for the valence electron polarizabilities calculated by Sternheimer.¹⁴ These polarizabilities differ from the measured ones¹¹ because of the polarization of the core electrons. It can be seen that the κ_{HZ} are all too small, ranging from 4% too low for K³⁹ to 19% too low for Na²³. However, even this simple theory, like all others, predicts that

$$k_{\text{Rb}87}/k_{\text{Rb}85} = \Delta\nu_{\text{Rb}87}/\Delta\nu_{\text{Rb}85}$$

in complete agreement with this experiment.

Column 4 lists the absolute shifts k that would be produced by an electric field of 1 kV/cm. These values are obtained from the measured κ 's and the theoretical result $k_{\text{Cs}133} = 2.248$ obtained in Ref. 5. The value listed here for K³⁹ agrees with the ex-

perimental result $k_{K^{39}} = 0.076(7)$ reported in Ref. 3.

Column 5 is the absolute frequency shift for an electric field of 1 kV/cm obtained from this experiment alone, independent of any theory. As discussed above, these numbers contain a 2% error from the electric field plate spacing d and filling factor s/l in addition to the statistical errors in the K^7 's. The two systematic errors are upper bounds, not standard deviations, and are large enough to include any possible line asymmetry.²

Finally, column 6 lists the shifts k_A obtained from the theory of Anderson, using revised energy level differences¹⁵ and valence electron polarizabilities of Ref. 14. Note that these shifts are all larger in magnitude than the experimental shifts, ranging from 20% too large for Na^{23} to 70% too large for Cs^{133} .

Independent evidence exists to support the correctness of the absolute shifts listed in column 4 of the table. Instead of using Cs^{133} as a reference to calibrate the interaction region, He^4 could be used. The Stark shift in the 3S_1 metastable state of He^4 has been measured¹⁶ and is in excellent agree-

ment with theoretical calculations.¹⁷ Furthermore, the calibration of the C region derived from the helium results agrees to better than 0.1% with that obtained here using cesium. Hence, there is complete consistency between the two independent theoretical calculations,^{5,16} the present measurements of the Cs^{133} Stark effect. Based on the helium calibration, the Stark shift of Cs^{133} measured in this experiment is

$$k_{\text{Cs}^{133}} = 2.25(1),$$

in excellent agreement with the calculated value $k_{\text{Cs}^{133}} = 2.248$.

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¹Not to be confused with the differential Stark shift (also quadratic in electric field strength) of the alkali transition $(I + \frac{1}{2}, -I + \frac{1}{2}) \leftrightarrow (I + \frac{1}{2}, -I - \frac{1}{2})$ reported in Ref. 9.

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